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PHOTOVOLTAIC EFFECT AND UTILIZATION OF
PHOTOVOLTAIC CELLS

Report Subtitle: Effect of Sub-threshold Electron
Radiation on Surface Properties of Ge P-V Cells

November 1, 1965 to May 31, 1966

BY

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Second Semiannual Report on
NASA Grant NGR-40-002-026

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Photovoltaic Effect and Utilization of Photovoltaic Cells

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Washington, D. C. 20546

Abstract

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The effect of high energy electron irradiation on the surface recombination properties of germanium p-n junction photovoltaic cells made by alloying appropriate impurities into wafers of various resistivities was investigated. The experiment was carried out with 250 keV electrons. This energy is well below the threshold energy for bulk damage in Ge (350 keV). It was found that the photovoltaic short circuit current had a strong dependence on integrated electron flux, on the time elapsed since the last irradiation, i.e. on the past history of the irradiated surface, on the pressure in the vessel in which the irradiation was performed, and on the resistivity of the material exposed to the electrons. For example, if the electrons were incident on the surface of 0.1 ohm cm n-Ge, the short circuit current I_s (which was inversely proportional to surface recombination velocity for the geometry of the cells) decreased by an order of magnitude after exposure to about $1200 \mu\text{coul}/\text{cm}^2$ (7.5×10^{15} electrons/ cm^2). Irradiation to higher fluxes did not lead to any additional changes, i.e. the effect had saturated. The relation between the experimentally observed changes and changes in more fundamental properties of the surface is discussed.

I. Introduction

Anyone who has studied radiation damage in semiconductors has encountered the problem posed by radiation induced changes in surface properties. The surface effect is characterized by reversibility without recourse to thermal annealing. The problem is usually obviated by radiation "conditioning" which in the case of electron irradiation consists of subjecting the specimen to electrons whose energy is below the threshold for bulk damage until the surface changes have saturated and one can then concentrate on bulk effects.

In an earlier study at Brown University^[1], an attempt was made to study the orientation dependence of electron bombardment radiation damage in n-type germanium with the help of p-n junction photovoltaic cells by following changes in the short circuit current I_{sc} associated with strongly absorbed light (8000 Angstroms, absorption constant $\alpha \sim 10^5 \text{ cm}^{-1}$). It was realized that I_{sc} was a strong function of surface recombination velocity in the case of such strongly absorbed light, but it was expected that surface "conditioning" would lead to a saturation of the surface changes and that the study of bulk damage could then proceed on the surface which had been passivated in this way. However, no such saturation was observed; the surface continued to change even after extremely high fluxes. Furthermore the changes were very large; the value of I_{sc} dropped by a factor of about 50 after exposure to a few hundred $\mu\text{coul/cm}^2$ of 200 keV electrons.

On the other hand, other early experiments at Brown^[2], showed that saturation of surface effects did occur on commercial silicon solar cells. It was found that irradiation of such cells by 100 keV electrons lead to an increase of surface recombination velocity s for n-Si and a decrease of s for p-Si. These effects were much smaller than those described above for Ge, but they indicated that s had to change by a factor of at least 10 in order to account for the observed 20 to 40% changes in I_{sc} .

No detailed investigations of the effect of high energy electron irradiation on semiconductor surface recombination velocity have been reported in the literature. There have, however, been two studies which are pertinent to this problem. In 1958, W. Spear^[3] studied surface conductance and the field effect in high resistivity n- and p-Ge at 80°K. He used electrons of various energies between 5 and 300 keV along with 4.5MeV electrons. He found that the surface conductance of n-Ge increased during irradiation while the surface conductance of p-Ge decreased. In 1964, Ovsiuk and Smirnov^[4] reported results of a study of the photoconductivity of high resistivity 40 ohm cm n-Ge irradiated by 1 to 16 keV electrons at 300°K. They were able to follow changes in surface recombination velocity by observing the changes in photoconductivity of thin samples. The light beam was modulated at a frequency of 300 cps and the change in the dc photoconductivity was monitored from the moment when the electron beam was switched on until it was switched off. It was found that the surface recombination velocity first decreased and then increased. The changes were attributed to a preliminary charge redistribution and a subsequent cleaning of the surface because of desorption of ions.

The experiments described in this report rely on analysis of photo-voltaic response to study radiation induced changes in surface recombination velocity. A detailed discussion of the underlying concepts has been given in the First Semiannual Report for the present grant (NGR-40-002-026) dated October 31, 1965.^[5] That report also describes the preparation of alloy junctions in Ge and Si, both n- and p-type and of various resistivities. The spectral response and current voltage characteristics of those cells is also recorded. This report is devoted to a description of the experiments performed on the n- and p-Ge cells.

II. EXPERIMENTAL ARRANGEMENT.

The experiment was carried out by using a Van de Graaff accelerator as electron beam source. The accelerating voltage was 250 keV. However, for the experiments performed in the vacuum of the Vac Ion Pumping System, the 250 keV electrons entered the experimental chamber by passing through a 0.0015" aluminum window. This resulted in a decrease in the average energy of the beam and gave rise to a spread in beam energy. In any case, the electron energy was well below the threshold for producing bulk defects in Ge (350 keV).

The beam current I_B was identified with the current absorbed by the sample, whose thickness (including the alloy dot) was sufficient to stop the beam. No correction was made for reflection of electrons from the surface. Usually the beam current was fed into an Elcor Integrator and the integrated charge received by the sample was determined in this way. Sometimes, however, the flux was computed from the current-time product. For most of the experiments, I_B lay between 10^{-7} A/cm². and 10^{-6} A/cm².

The samples were mounted on metallized Al₂O₃ wafers which were soldered to a water cooled copper block. The Al₂O₃ provided electrical insulation from and thermal contact with the copper block. The temperature was monitored with the help of copper constantan thermocouples attached to the irradiated sample. The temperature stayed around 5°C and it did not change by more than a few degrees during irradiation. Control experiments were used to determine how much of a temperature difference could be tolerated by the specimens. These experiments involved delivery to the junction of an amount of electrical power equivalent to the amount delivered by the electron beam for a time equivalent to that involved in the irradiation. It was found particularly in the case of high resistivity specimens that a few tenths of

a degree caused substantial changes in I_{sc} and the maximum beam current was so chosen as to insure that the temperature did not exceed tolerable limits.

A tungsten lamp combined with a filter consisting of a copper chloride solution served to provide strongly absorbed light, i.e. the absorption constant α in Ge was greater than 10^4 cm^{-1} for this combination of lamp and filter. This guaranteed that the light absorption was confined to a thin layer near the surface whose thickness was less than 1 micron. The electron beam was incident normal to the surface; the light was reflected onto the surface at nearly normal incidence by a front surface mirror (See Fig. 1).

The samples were situated in a pyrex glass cross pumped by a Vac Ion pump, sorption jumps being used to provide the fore-vacuum. This system was almost free of organic vapors; only the neoprene gaskets on the glass cross were a potential source of such vapors. The reason for recourse to an organic vapor free vacuum was the suspicion that irradiation in the presence of organic vapors can lead to the deposit of carbon and carbon compounds on the semiconductor surface. Such deposits could conceivably dominate any other effects of radiation on the surface and were therefore clearly undesirable.

The response of the cells to both constant and modulated light was measured. A load resistor was connected across the sample, its value so chosen that the signal was proportional to I_{sc} . The illumination level was such that the i - V characteristic was linear, i.e., $V < \frac{kT}{e}$. The voltage produced by constant illumination was amplified by a Kiethly dc amplifier whose output versus time was in turn displayed on a Moseley x-y plotter. The ac voltage produced by modulated light was amplified by a low noise Tektronix ac amplifier whose output was displayed on a Hewlett-Packard ac voltmeter.

III. DEPENDENCE OF I_{sc} ON LIGHT INTENSITY

It was found that the response was a function of the intensity of light incident on the sample. For example, in the case of a 0.1 ohm cm p-Ge cell resting in a vacuum of 2.5×10^{-7} torr, it was found that the value of I_{sc} increased by a factor of three after about 15 minutes of continuous exposure to "high intensity" light (Fig. 2). If the illumination, continued for a long enough period, the response eventually saturated. The intensity of the light was not measured; only the voltage applied to the tungsten lamp was measured. It was found that if the light intensity were kept low enough, the signal did not change with time though it was large enough to be easily measurable. Thus we had the choice of either using "low intensity" which did not change I_{sc} over the period of the experiments or of using "high intensity" light and allowing saturation to set in before proceeding with irradiation. Our experiments were performed in one or the other of these stable modes of behavior.

IV. DEPENDENCE OF I_{sc} ON PRESSURE

Figure 3 shows the dependence of I_{sc} on pressure for a 20 ohm cm n-Ge sample. The sample had been previously irradiated and allowed to rest in a vacuum of 5×10^{-7} torr for a period of hours. Then one atmosphere of dry nitrogen was admitted into the experimental chamber with the results shown in Fig. 3. The light was set for "high intensity" i.e. effects associated with light intensity had been allowed to saturate prior to the measurement shown in the figure. After four hours the response had increased by a factor of more than two. At this time, the sorption pump was turned on and the response decreased. The Vac Ion Pump was turned on after about 2 hours and the response continued to fall to its original value although the return required another 12 hours.

The irradiations were performed with a pressure of about 5×10^{-7} torr after sufficient time had elapsed to stabilize the surface.

V. EFFECT OF ELECTRON IRRADIATION ON I_s

Having established that the surface was stable as a function of time if the pressure was maintained constant at or below 10^{-6} torr and if the light intensity were kept constant at a low intensity or at a high intensity after saturation had been allowed to occur, we proceeded with the irradiation according to the following scheme. The samples were irradiated to a selected flux usually of the order of tens or hundreds of $\mu\text{coulombs}/\text{cm}^2$. The beam was interrupted by means of an electrically operated shutter, a measurement was made very rapidly and the irradiation was resumed. Rapid measurement was essential after control experiments had established that the response changed with time after interruption of the electron beam as shown in Figs. 4 and 5 for 0.1 ohm cm p-Ge and 30 ohm cm n-Ge respectively. In both cases, I_{sc} changed by about 50% within five minutes after irradiation. This "annealing" added to the complexity of the experiment.

The measurements described herein were performed with both constant and modulated light; no significant difference was observed between these two modes of performing the experiment. The modulation frequency was as high as 300 cps.

Both annealing and irradiation induced changes were functions of the resistivity of the bulk material whose surface was irradiated. Figures 6 through 11 show plots of normalized I_{sc} vs integrated flux received by the samples.

Figures 6 and 7 pertain to low resistivity (0.1 ohm cm) p-Ge diodes made on wafers cut from the same Ge crystal. The first of these diodes was irradiated in the vacuum of the Van de Graaff machine. The second was irradiated in the vacuum produced by the Vac Ion pump. Each of the figures shows three curves. All the data were taken with "low intensity" illumination. The samples were allowed to rest for periods of a few hours between curves. During this time, some annealing had occurred. It was obvious that the behavior of I_{sc} during a given irradiation was a function of the annealing time and previous irradiation history of the sample, but it was not possible to select an annealing time which would lead to consistently reproducible irradiation curves. Figures 6 and 7 suggest that a sample irradiated in the Van de Graaff vacuum and one irradiated in the Vac Ion vacuum behave differently. However, the beam currents differed by an order of magnitude for these two irradiations ($I_B \sim 1.0 \times 10^{-6} \text{ A/cm}^2$ in Fig. 6 and $9 \times 10^{-8} \text{ A/cm}^2$ in Fig. 7) and it is possible to ascribe some of the difference to this difference in beam current. In the case of the sample irradiated in the Van de Graaff vacuum, I_{sc} increased by as much as 40% during the early part of the irradiation, reached a maximum and then decreased. This is similar to the behavior reported by Ovsyuk and Smirnov for 40 ohm cm n-Ge. This increase in I_{sc} in the early part of the curve may be related to the increase caused by high light intensity shown in Fig. 2. Prolonged irradiation caused the effect to saturate. However, the value of the saturation relative to the original value was a function of the previous irradiation history of the specimen. In general, the saturated value was lower in successive runs performed within a few hours of each other.

In the case of the low ρ p-Ge sample irradiated in the Vac Ion vacuum, no initial increase of I_{sc} was observed (Fig. 7). In general, these irradiations showed an initial rapid decrease followed by an increase which did not saturate at the maximum fluxes used in this irradiation. However, note that the total integrated flux in Fig. 7 is a factor of seven smaller than in Fig. 6.

Figure 8 shows a series of curves taken on 10 ohm cm p-Ge irradiated in the Vac Ion vacuum. These curves all showed an initial increase in I_{sc} and a subsequent decay toward a saturated value.

In the case of 30 ohm cm n-Ge irradiated in the Vac Ion system, I_{sc} increased by as much as 80% and then saturated (Fig. 9) after a flux of about $1500 \mu\text{coul}/\text{cm}^2$.

Figure 10 shows a series of curves for 9 ohm cm n-Ge. These show an initial dip in I_{sc} followed by an increase to a saturated value. Note that the total integrated flux on this curve is rather low.

Finally, Fig. 11 shows the results of successive irradiation of a $0.1 \Omega\text{cm}$ n-Ge specimen in a vacuum of 4×10^{-7} torr in the Vac Ion system. In this case I_{sc} drops by an order of magnitude after about $1500 \mu\text{coul}/\text{cm}^2$ and then attains a stable saturated value.

To summarize, the samples exhibit rapid changes during the first $1500 \mu\text{coul}/\text{cm}^2$ (about 1×10^{16} electrons/ cm^2) and then saturate. If we exclude Fig. 6, which was taken in the Van de Graaff vacuum, the asymptotic value of I_{sc} is greater than the initial value for two high ρ n-Ge samples (9 and 30 ohm cm n-Ge); no more than 20% below the initial value for two p-samples (0.1 and 10 ohm cm p-Ge) and an order of magnitude below the initial value for the low ρ (0.1 ohm cm) n-Ge sample.

VI. DISCUSSION

Analysis of I_{sc} for strongly absorbed light and plane parallel geometry leads to the expression

$$I_{sc} = \frac{2qN_0(1-R)}{\left[\frac{Ls}{D} + 1\right]} \quad (1)$$

where q is the electronic charge; N_0 the number of incident photons; R is the reflection coefficient; L is the diffusion length; D is the diffusion constant and s is the surface recombination velocity.

If $\frac{Ls}{D} \gg 1$, I_{sc} is inversely proportional to s . For the p-Ge samples used in our experiments $L \sim 10^{-1}$ cm; $D \sim 90$ so that $s \gg 1000$ before we can neglect unity in the denominator. For the n-Ge samples $D \sim 45$ so that $s \gg 500$ would satisfy this condition. Furthermore, if it is assumed that irradiation changes s by changing the density of surface states, then s will be a function of flux and one can write very approximately^[4]

$$s(\phi) = s_0 + a N_{sr}(\phi) \quad (2)$$

where s_0 is the initial value of s , a is a constant and N_{sr} is the density of recombination centers which is of course a function of ϕ . In writing Eq. (2), it is assumed that the bands do not bend as a result of irradiation and that only one kind of surface state is involved in s . Then

$$\frac{1}{I_s(\phi)} = \frac{1}{A} + \frac{L}{D} s_0 + \frac{L}{D} a N_{sr}(\phi) \quad (3)$$

where $A^{-1} = 2 q N_0 (1-R)$. Plots of $[I_s(\phi)]^{-1}$ were made from the data of Figs. 6 through 11. Except for Fig. 11 (0.1 ohm cm n-Ge) none of the plots were straight lines, i.e. $N_{sr}(\phi)$ was not a linear function of flux. It was proposed by Ovsyuk and Smirnov^[4] that

$$N_{SR}(\phi) = N_{SR}(0) \exp \left[-\frac{\sigma\phi}{e} \right] \quad (4)$$

where σ is the cross section for dislodging an atom. This relation was applied to the data in Figs. 6 through 10. It was assumed that the concentration of surface states was approaching an asymptotic value. The difference between $\frac{1}{I_{sc}}$ and the asymptote was then plotted against flux. In the case of 0.1 ohm cm p-Ge (Fig. 6) and 10 ohm cm p-Ge (Fig. 8) in which I_{sc} decayed toward an asymptote that Eq. (4) fitted the data. However, in the case of 9 ohm cm n-Ge (Fig. 10) and 30 ohm cm n-Ge (Fig. 9) in which I_{sc} rose to a saturation value, Eq. (4), or rather its companion equation

$$N'_{sr}(\phi) = 1 - N(0) \exp \left[-\frac{\sigma\phi}{e} \right]$$

did not fit the data. Consequently, the relatively simple explanation of the phenomenon offered by Ovsyuk and Smirnov^[2] may sometimes fit the data but it certainly can not be applied to all the resistivities which we studied.

To summarize, the latter portions of the I_{sc} vs ϕ curves which may be associated with desorption of atoms from the Ge surface yield information about the behavior of surface recombination velocity s vs ϕ . In general, this relation is complex and cannot be fitted into any simple theory.

As regards the initial parts of I_{sc} vs ϕ curves, especially the reverse behavior shown in Figures 6 and 8, the data are virtually impossible to reproduce in successive runs. This being the case, there is little reason for attempting to fit it into any sort of simple expressions. It is very likely that there are two processes occurring in every case, even in situations like those shown in Figs. 9 and 11 where no reversal in the direction of I_{sc} occurs. In those cases, it is possible to distinguish a

more rapid change in the early segment of the curve and a subsequent slower change. It has been suggested in Ref. (4) that the early segment of the curve reflects "charge redistribution among surface states". On the basis of our data, we cannot refute or support such an assertion. We do, however, call attention to the effects associated with "high light" intensity shown in Fig. 2. The light involved has photon energies in excess of the band gap and it is possible that such light is able to liberate electrons from surface states or to excite electrons into such levels. Radiation can also perform this function. It is, therefore, proposed that the initial segments of the I_{sc} vs ϕ curves reflect an approach to saturation of the same genre as the approach to saturation which accompanies "high light" illumination of the surface.

As for the annealing of irradiated surfaces shown in Figs. 4 and 5, this is probably associated with re-absorption of atoms on the Ge surface. It should be a function of the atomic species in the medium surrounding the specimen. Some preliminary experiments have shown that moist air induces much more rapid annealing than dry air or dry nitrogen. The annealing process requires further study.

VII. CONCLUSIONS

1. The influence of 250 keV electron irradiation on the surface recombination velocity of n- and p-Ge was investigated.

2. It was found that the response of the cells was a function of the temperature, light intensity, pressure and possibly of the amount of organic vapors in the medium surrounding the specimens.

3. Even after ways were found to obviate the effects of these parameters, it was found that it was not possible to reproduce I_{sc} vs ϕ curves in successive runs. Nor did the behavior of I_{sc} vs ϕ ever settle into a reproducible pattern even after a large number of successive runs.

4. In general, the I_{sc} vs ϕ curves exhibited two portions. One was a rapidly changing initial portion in which I_{sc} could change in a direction opposite to that observed in the second, later portion of the curve.

5. The later portion usually exhibited saturation of s at integrated flux values of about 1.5×10^{-3} coul ($\sim 1 \times 10^{16}$ electrons/cm²). The final value of s was greater than or lower than its initial value depending mainly on the resistivity of the base material. However, the amount of change and the direction of the change did not change in a systematic way as the resistivity changed from low ρ p-Ge through intrinsic to low ρ n-Ge. The largest change observed was in 0.1 ohm cm n-Ge, in which the saturation value of I_{sc} was an order of magnitude smaller than the initial value.

The largest increase in I_{sc} was that observed in 30 ohm cm n-Ge where the asymptote was about 1.8 times the initial value i.e. s had decreased by a factor of 1.8.

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FIGURE CAPTIONS

- Fig. 1 Experimental Arrangement
- Fig. 2 Short circuit current I_{sc} (arbitrary units) vs time showing the effect of "high intensity" illumination in p-type Ge $\rho = 0.1$ ohm cm. Vacuum 5×10^{-7} torr.
- Fig. 3 I_{sc} vs time, after saturation of "high intensity" illumination, showing the effect of pressure on I_{sc} . Sample had previously been irradiated in a vacuum of 5×10^{-7} torr.
- Fig. 4 I_{sc} vs time after interruption of 250 KeV electron irradiation. This plot shows the "annealing" of p-Ge, $\rho = 0.1$ ohm cm. in a vacuum of 5×10^{-7} torr.
- Fig. 5 Same as Fig. 4 except that the diode was made on n-Ge, 30 ohm cm.
- Fig. 6 I_{sc} vs flux of 250 keV electrons. The flux values must be multiplied by 5 to get $\mu\text{coul}/\text{cm}^2$. Curves show three successive runs. Note that the curves are normalized; the initial values are not equal. Van de Graaff vacuum (oil diffusion pumps $p \sim 10^{-6}$ torr).
- Fig. 7 Same as Fig. 6 for p-Ge-0.1 ohm cm. and Vac Ion pump vacuum $p \sim 5 \times 10^{-7}$ torr.
- Fig. 8 Same as Fig. 6 for p-Ge $\rho = 10$ ohm cm. Van Ion Vacuum $p \sim 5 \times 10^{-7}$ torr.
- Fig. 9 Same as Fig. 6 for n-Ge, $\rho = 30$ ohm cm., Vac Ion Vacuum, $p \sim 5 \times 10^{-7}$ torr.
- Fig. 10 Same as Fig. 6 for n-Ge, $\rho = 9$ ohm cm. Vac Ion Vacuum, $p \sim 5 \times 10^{-7}$ torr.
- Fig. 11 Same as Fig. 6 for n-Ge, $\rho = 0.1$ ohm cm. Van Ion Vacuum, $p \sim 5 \times 10^{-7}$ torr.

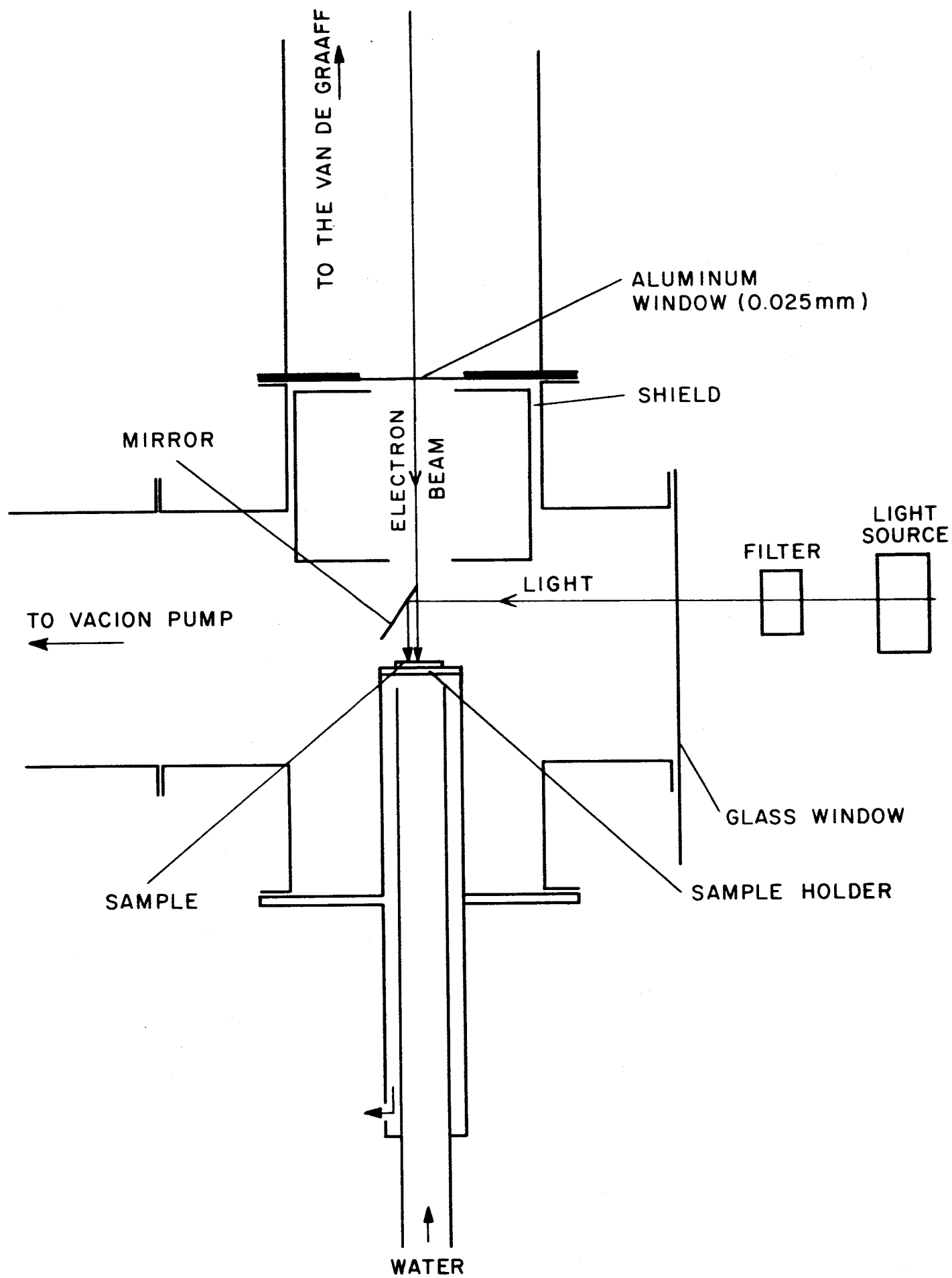


FIGURE 1

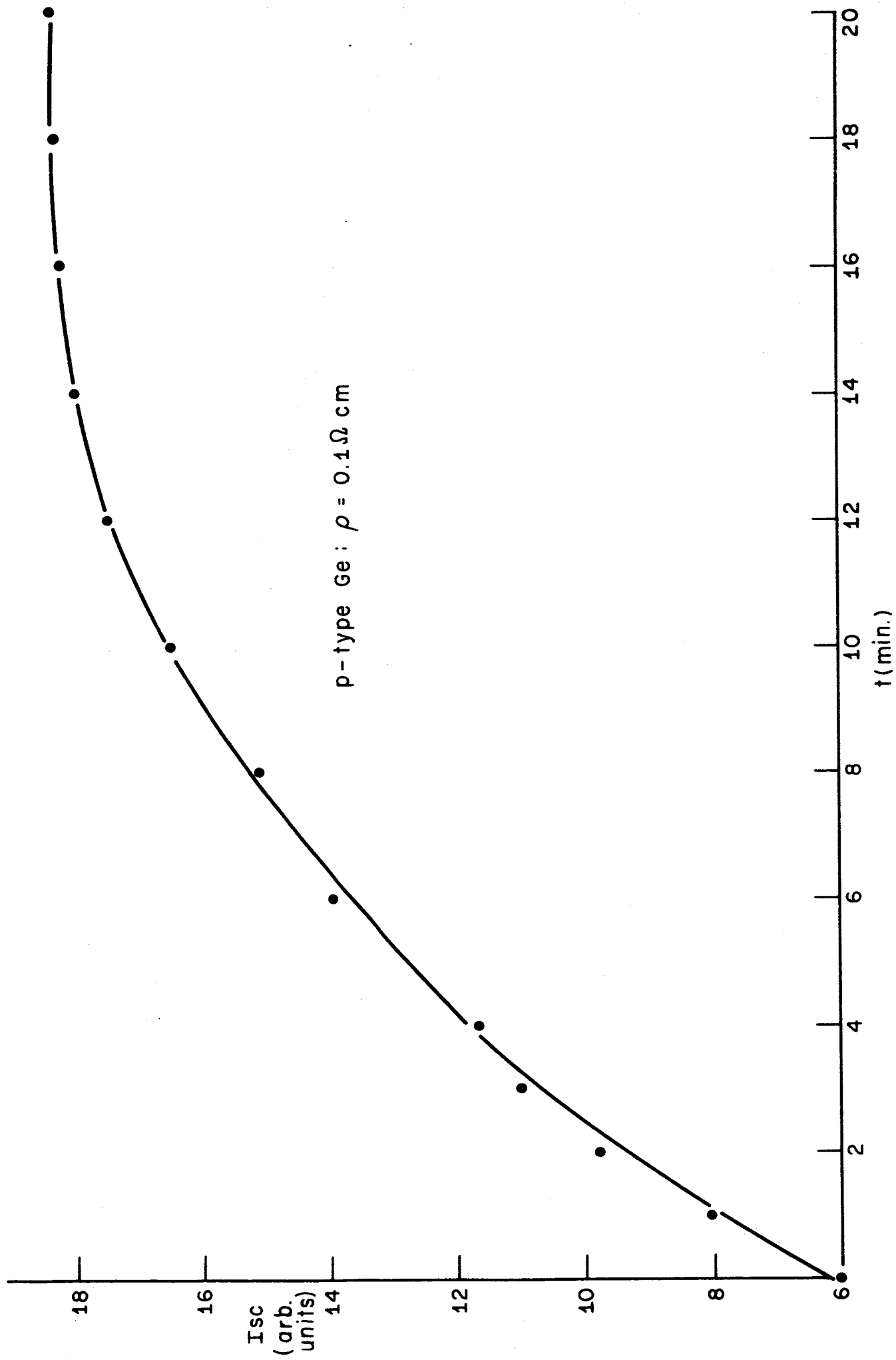


FIGURE 2

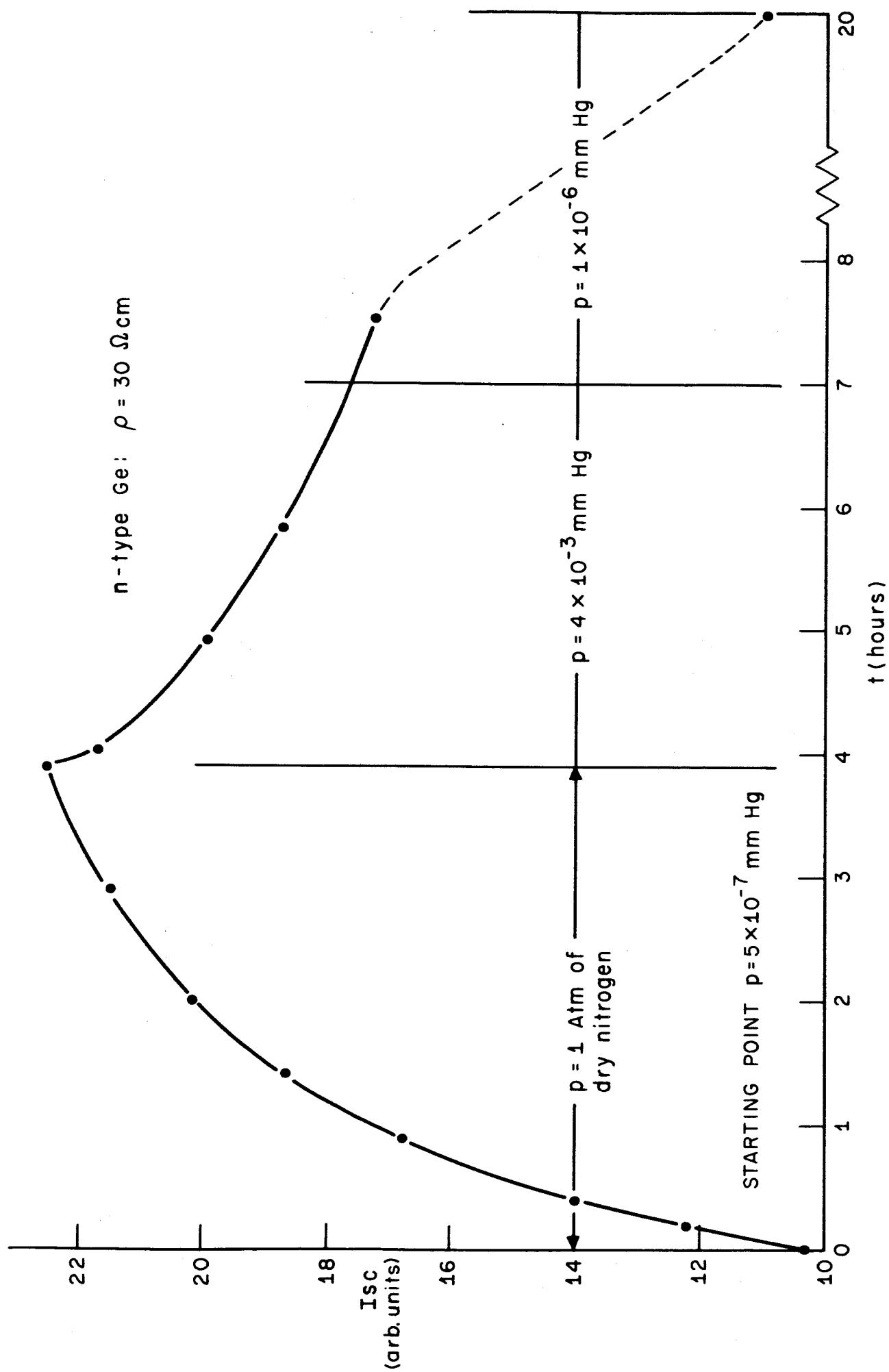


FIGURE 3

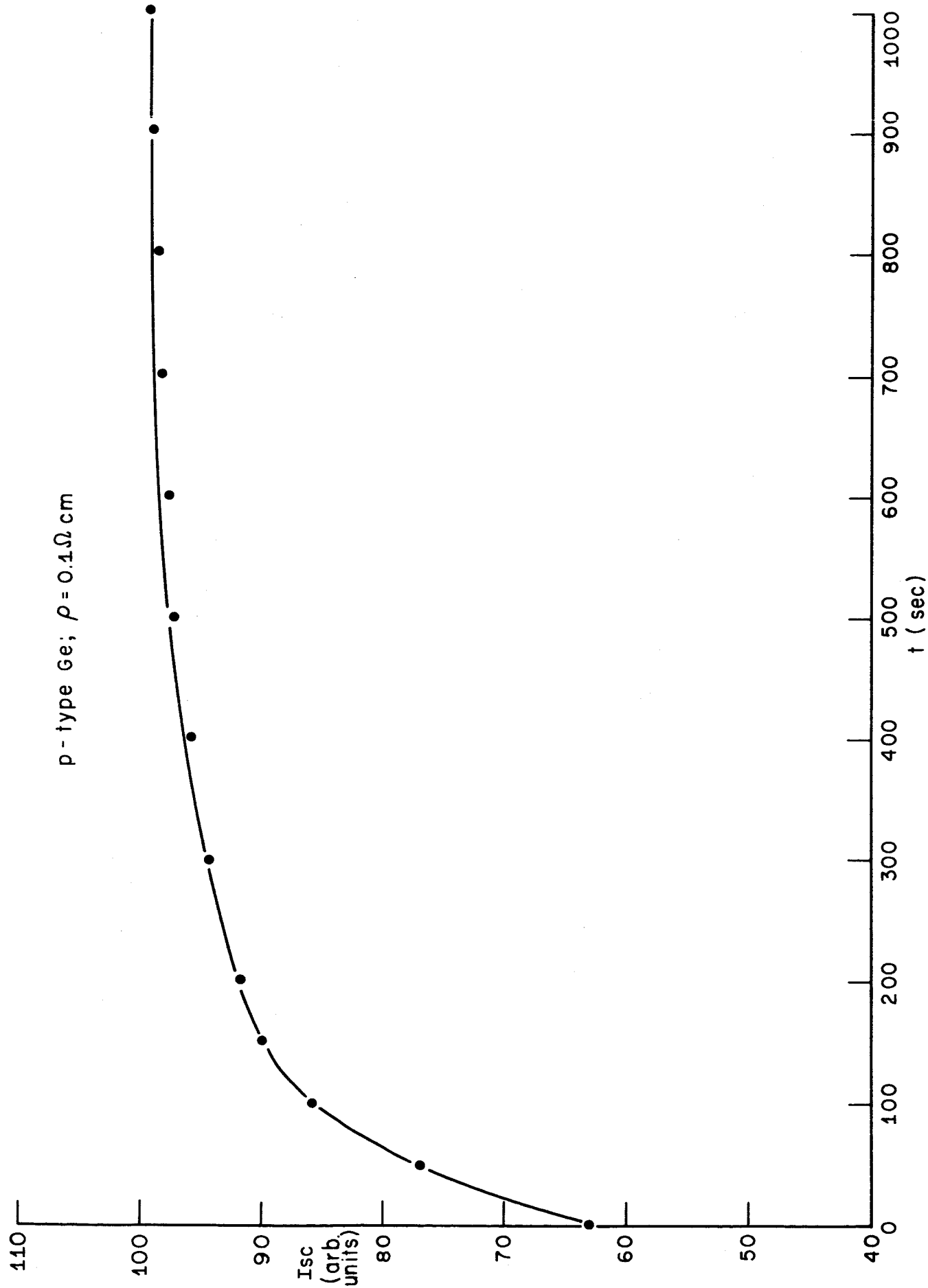


FIGURE 4

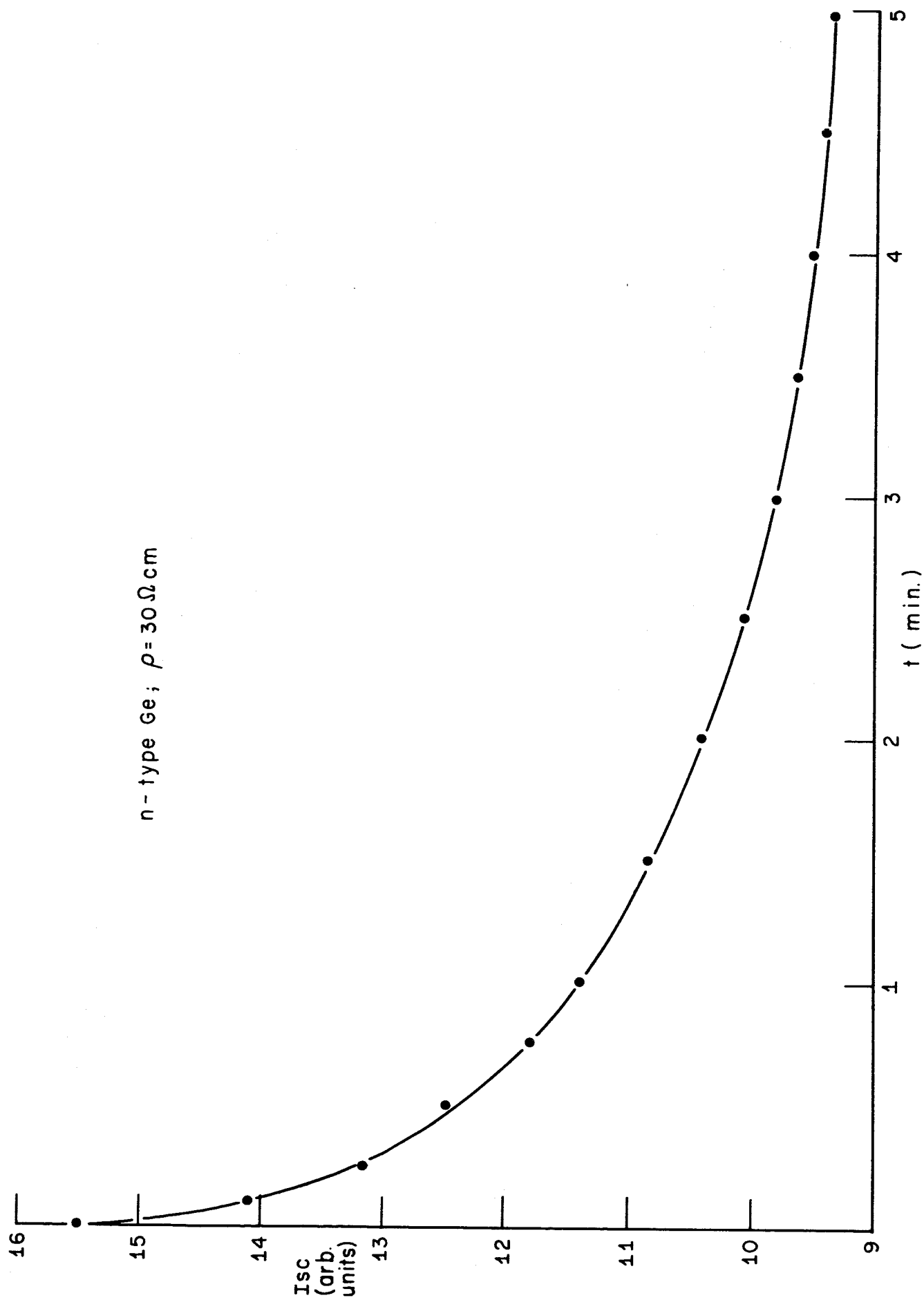
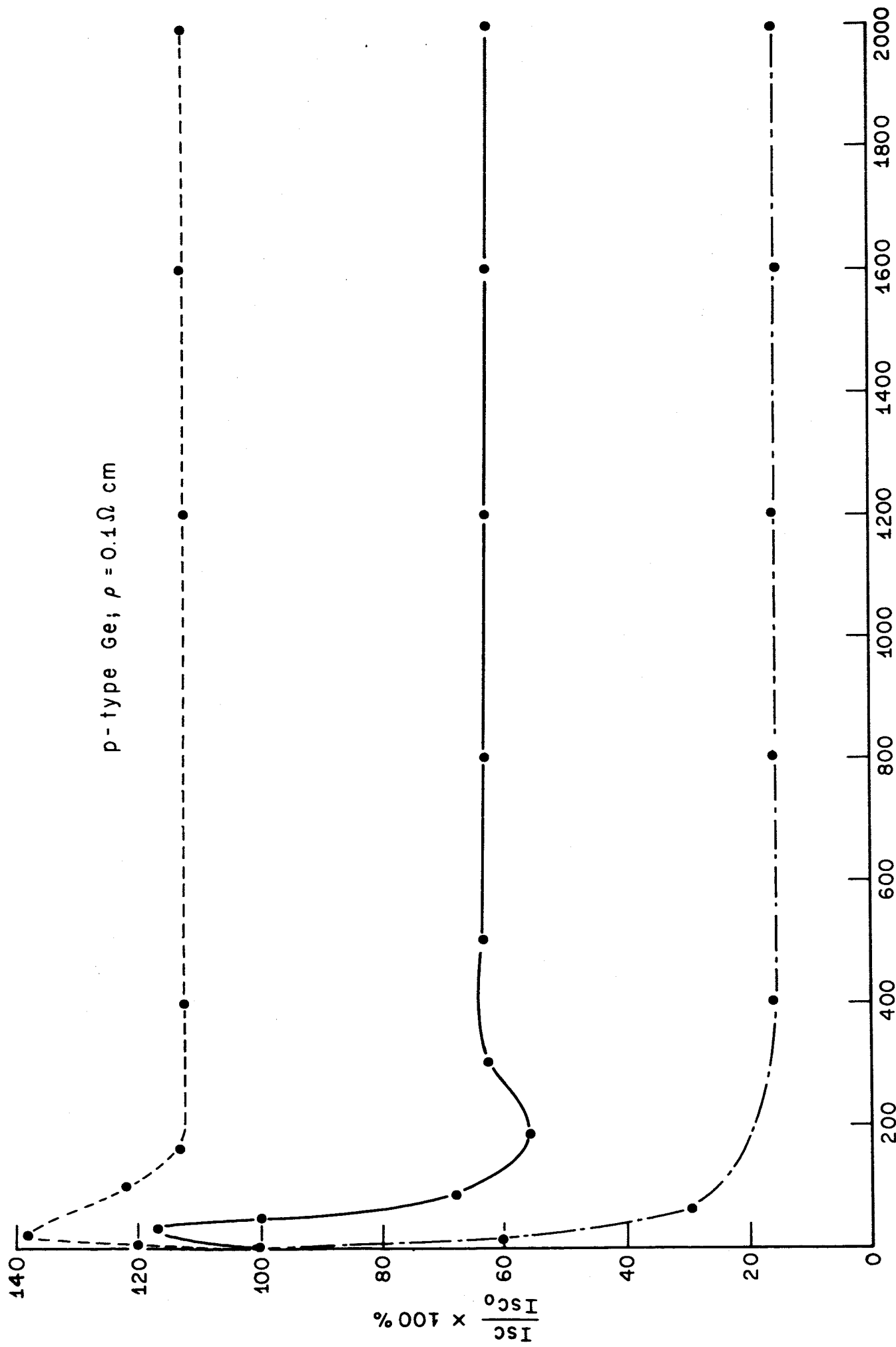
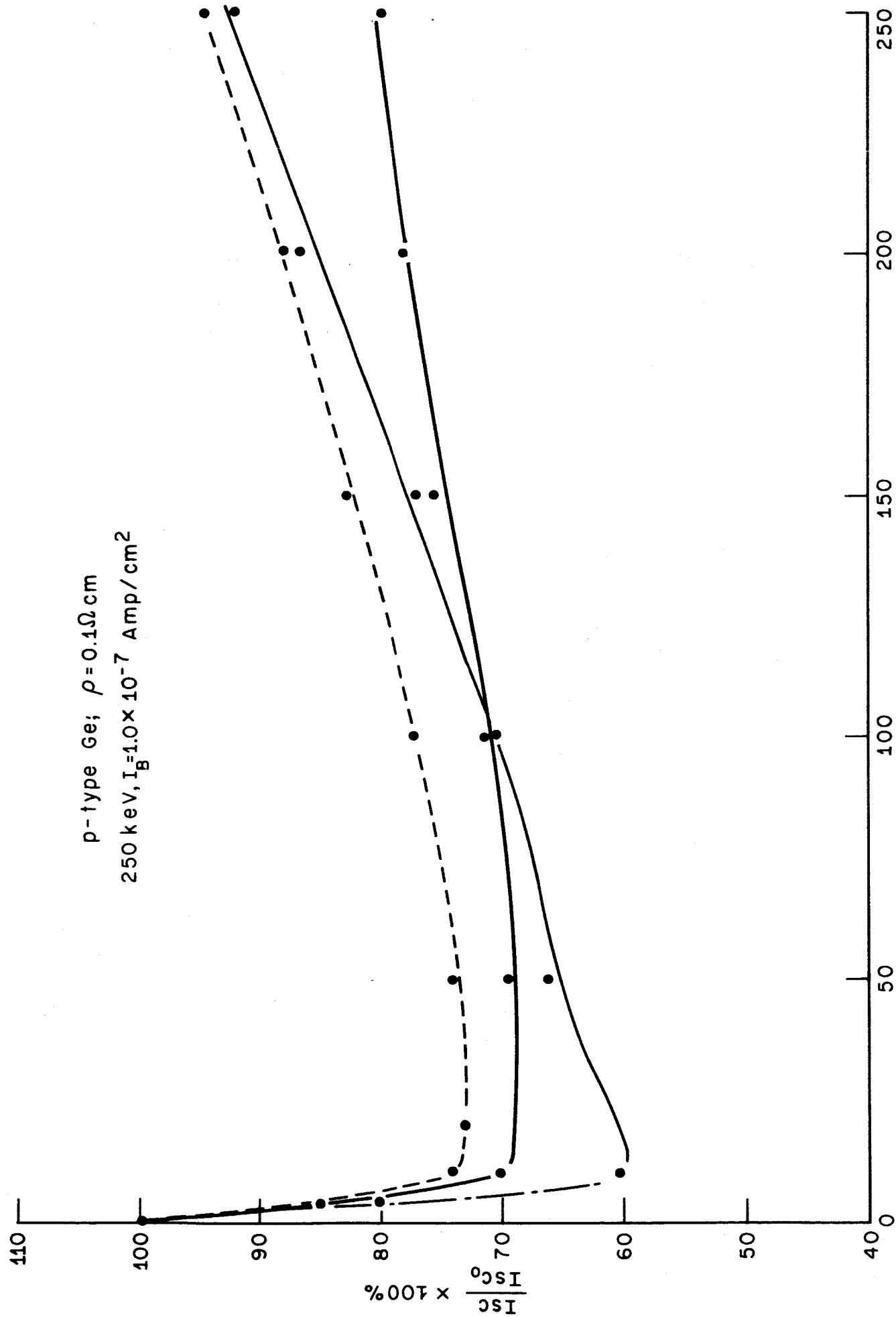


FIGURE 5



FLUX ($\mu \text{ coul}$)

FIGURE 6



FLUX ($\mu \text{ coul}$)

FIGURE 7

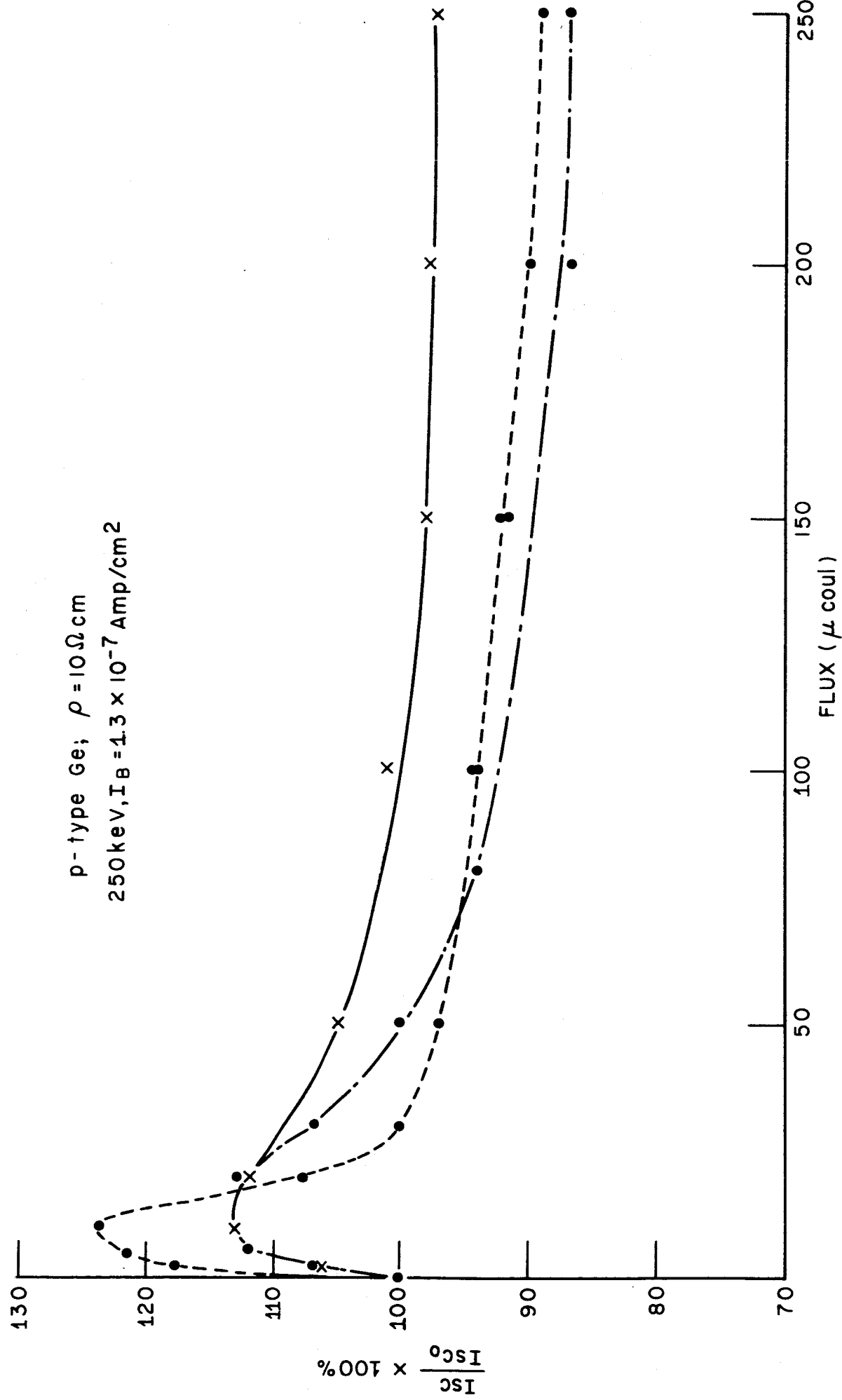


FIGURE 8

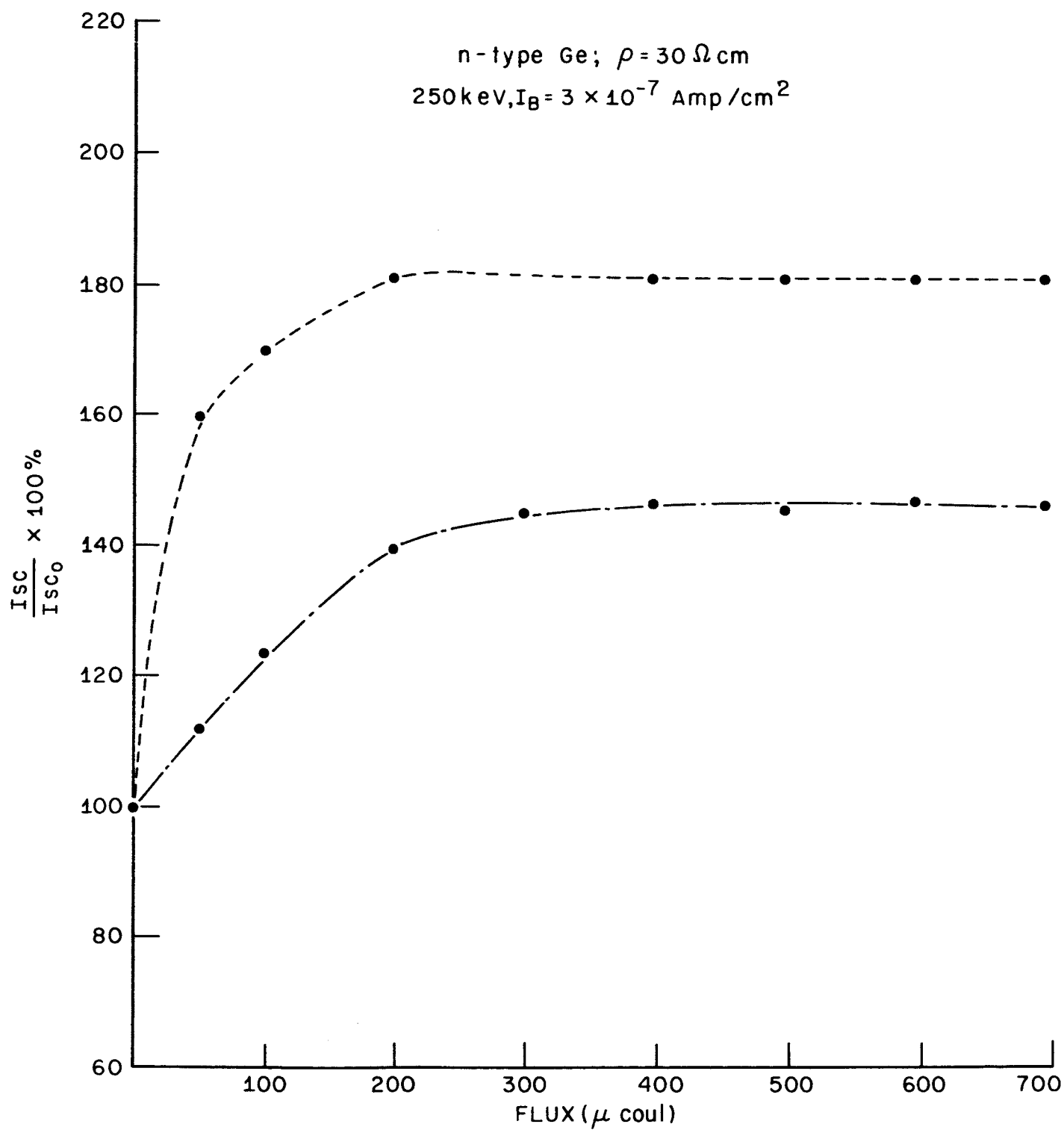


FIGURE 9

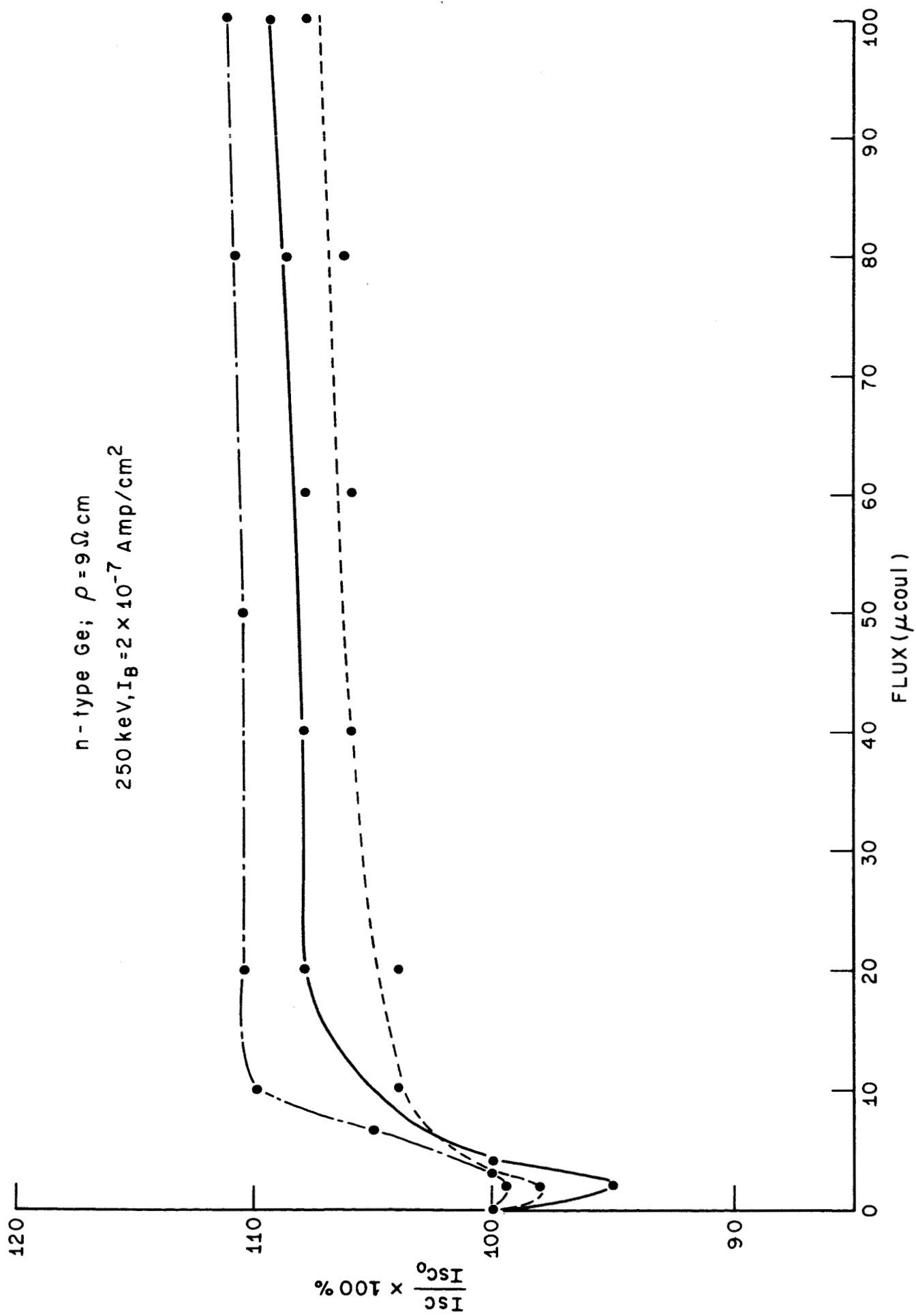


FIGURE 10

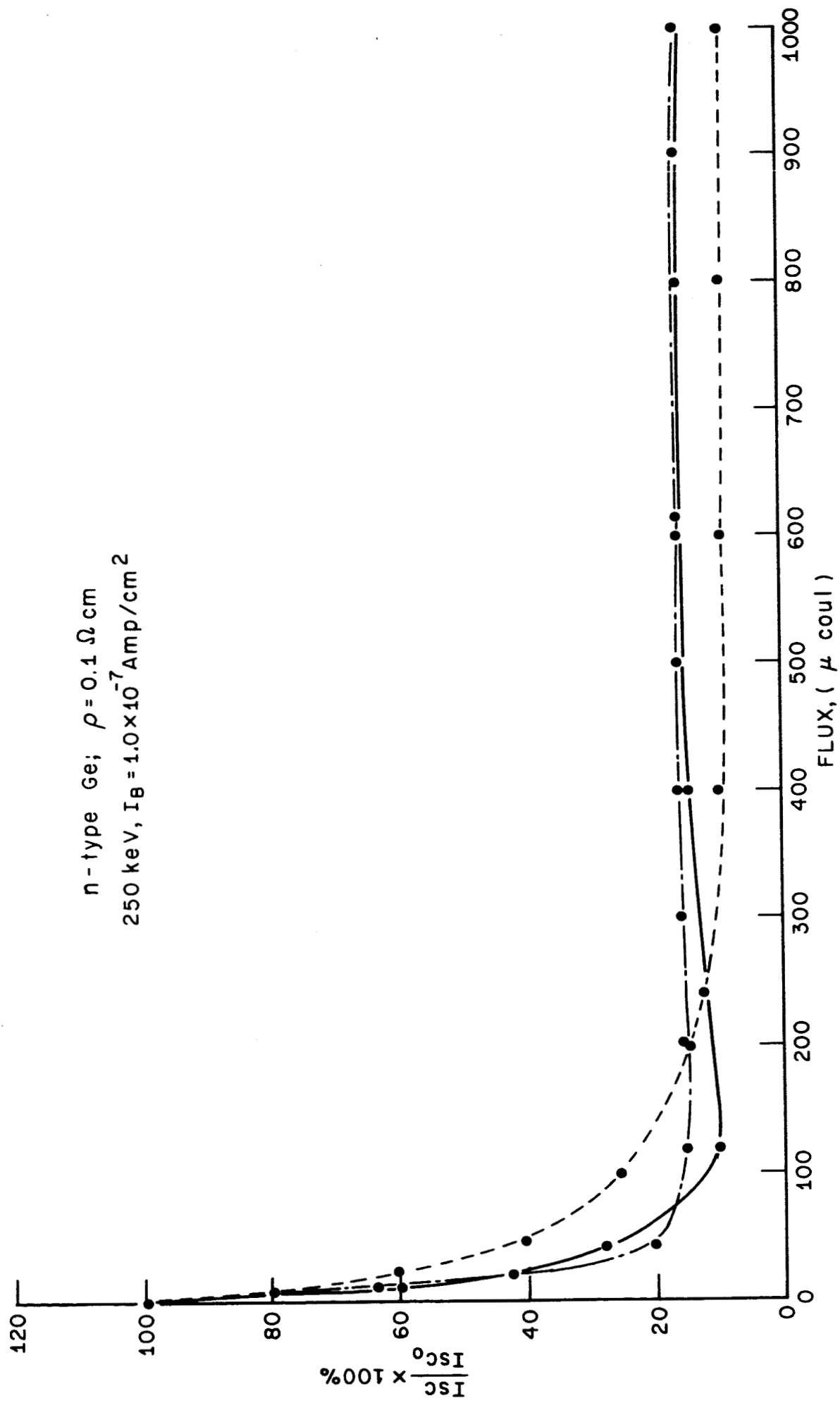


FIGURE 11